Intermetallics 77 (2016) 14–22

Contents lists available at ScienceDirect

Intermetallics

journal homepage: www.elsevier.com/locate/intermet

Heat capacity of η-AlFe (Fe_2Al_5)

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ARTICLE INFO

Article history:
Received 3 March 2016
Received in revised form
30 June 2016
Accepted 5 July 2016
Available online 16 July 2016

Keywords:
Aluminides
Order/disorder transformation
Thermodynamic properties
Density functional theory
Ab–initio calculations
Differential scanning calorimetry

ABSTRACT

The heat capacity of Fe_2Al_5 was calculated using first principle methods and was measured on four compositions between 71.17 at.% Al and 72.17 at.% Al in the temperature range between 235 K and 1073 K. An order/disorder reaction in η-AlFe was found occurring in the range between 523 K and 553 K. Excellent agreement between the calculated and measured c_p values were found for the ordered η-AlFe phase whereas the calculated heat capacity is slightly smaller in comparison to the c_p of the disordered phase.

1. Introduction

The Al-Fe system is an important part of commercial Al-alloys, which are high order systems. However, even small amounts of Fe causes formation of intermetallic compounds which substantially influence the mechanical properties of alloys. The Al-Fe system also presents theoretical interests because of several transitions between the disordered phase A2 (SG #229, $Im\bar{3}m$) and the ordered phases B2 (SG #221, $Pm\bar{3}m$) and $D0_3$ (SG #225, $Fm\bar{3}m$) in the Fe-rich side, e.g. A2 ↔ B2, A2 ↔ $D0_3$ and D0 ↔ B2 [21,30].

The Al-Fe system was experimentally investigated many times using phase equilibrations and thermal analysis. Experimental thermodynamic data are also available, such as enthalpies of formation of intermetallic compounds, mixing enthalpy in liquid phase and chemical potential. The detailed review of experimental studies can be found in Ref. [21]. Since the evaluation of Kattner and Burton, several new experimental researches have been published [3,23,18]. Additionally thermodynamic parameters of the Al-Fe system were assessed in several works [21,30,17]. The substantial role of ab-initio calculations for the CALPHAD type assessment was stressed by Ref. [30]. Enthalpy of formation for FeAl and Fe_3 Al phases were calculated by first principles [22]. It should be noted that in spite of extensive experimental and theoretical studies of the Al-Fe system, the heat capacity above room temperature of the intermetallic compounds $FeAl_2$, Fe_2Al_5 and Fe_4Al_3 have not been measured so far [19]. It should be mentioned that heat capacity for Fe_2Al_5 was reported only in the temperature range between 1.8 K and 300 K [7]. Theoretical calculations of c_p are also not available. The additive Neumann-Kopp rule was used to estimate heat capacity in the works presenting a CALPHAD assessment [21,30]. Substantial drawback of the Neumann-Kopp approach is that the phase transformations occurring in elements will be present in the intermetallic as well. For example, change of c_p due to melting will be observed in the c_p curve of intermetallic compounds which melts at substantially higher temperature than pure Al. The phase transformations in Fe will be also seen in intermetallics. Therefore, it is very important to measure the heat capacity of intermetallic compounds in the range from room temperature up to high temperatures to have a reliable extrapolation of enthalpy of formation and standard entropy functions to high temperature range.

The phases in Al-rich region such as ζ ($FeAl_2$), η (Fe_2Al_5) and θ

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http://dx.doi.org/10.1016/j.intermet.2016.07.002

($FeAl_3$) have some small but distinctive homogeneity ranges to be easily synthesised as single phase. Therefore they present interest for measurement of heat capacity and comparison with ab-initio calculations. From the other side compounds with rather small elemental cells need to be selected for ab-initio calculations. Based on the above consideration, the phase Fe_2Al_5 has been selected for heat capacity measurements and ab-initio calculations.

The aim of the present work is to measure the heat capacity of the η-AlFe intermetallic phase (Fe_2Al_5) and compare these results with ab-initio calculated data to confirm reliability of such calculations.

2. Experimental methods

2.1. Sample preparation

Samples with three nominal compositions (S1 71.17 at.% Al, S2 71.67 at.% Al and S4 72.17 at.% Al) within the homogeneity range of η-AlFe were prepared by arc melting (AM furnace, Edmund Bühler GmbH, Hechingen, Germany) using pure metals (Al 99.9999; Fe 99.995; Alfa Aesar, Karlsruhe, Germany). The sample S3 (71.7 at.% Al) was prepared by levitation melting followed by casting in a cold copper mould [23].

The as-cast samples were sealed in evacuated and argon back-filled silica glass tubes. The samples were then annealed at 1273 K for seven days and furnaced cooled to room temperature to get a homogeneous microstructure with grains which will not grow during the heat capacity measurements. A disc with a height of $\approx$1.5 mm and a diameter of 5 mm was cut from each annealed sample. The discs were grinded and polished and were proved to be single phase by SEM investigations.

2.2. Sample characterisation

The different samples were characterised by means of microstructure investigation and composition measurements using SEM combined with EDX (Leo1530, Carl Zeiss with EDX from Bruker AXS) and EBSD. Samples were also investigated by X-ray diffraction using a URD63 diffractometer (Seifert-FPM, Freiberg/Germany) with Cu $K\alpha_1$ radiation.

A typical microstructure of the samples is shown in Fig. 1. Several EBSD patterns were obtained from different grains. All EBSD-patterns were indexed using the orthorhombic Fe_2Al_5 structure reported by Burkhardt et al. [5].

2.3. DTA measurements

The melting point of all samples were determined by DTA (Setsys 1750, Setaram, France). Temperature calibration was made using melting points of the standard materials Al, Au and Ni with heating rates 2, 5 and 10 K/*min*. The measurements were done under Helium atmosphere in Al_2O_3 crucibles. The samples were heated from room temperature to 1273 K with 20 K/*min*, then isothermal held for 5 h and finally heated with 5 K/*min* above the melting point.

2.4. Heat capacity measurements

The heat capacity of all samples were measured between 235 K and 1073 K under argon atmosphere. A DSC 8000 (Perkin Elmer, USA) was used for the temperature range from 235 K to 823 K. Temperature calibration was made using melting points of standard materials In and Pb. All measurements were done in aluminium crucibles and with a heating rate of 10 K/*min*.

A Micro-DSC II (Setaram, France) was used for measurements of sample S2-I between 293 K and 353 K. The heat capacity was determined with the step method using temperature steps of 1 K. The error was 0.5% for all temperatures.

A DSC 404C Pegasus (NETZSCH-Gerätebau GmbH, Selb, Germany) was used for the temperature range from 293 K to 1073 K. Temperature calibration was done using the melting points of Al, Sn, Zn, Ag and Au. Platinum crucibles with a platinum lid and an alumina inlay were used in the experiments. Depending on temperature, the heat capacity was determined from temperature scans with heating rates of 2, 5 and 10 K/*min*.

The heat capacity was determined with the continuous method described by Gatta et al. [12] using sapphire as standard material for measurements done with the DSC 8000 and DSC 404C. The determined heat capacity data can be fitted by

$$c_p(T) = a + b \cdot T + \frac{c}{T^2} \ , \qquad (1)$$

where a, b and c are adjustable parameters and T is the temperature. The determined values of the heat capacity will be given in per mole of atoms.

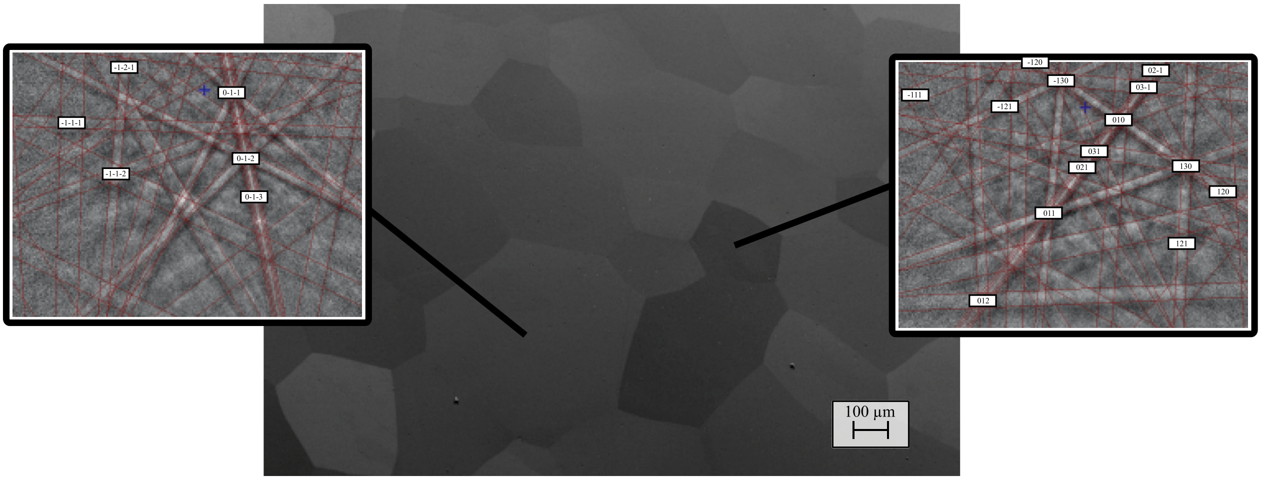

Fig. 1. Single phase (η-AlFe) SEM-micrograph (BSE) of the annealed S2-I (71.67 at.% Al) sample after heat capacity measurements together with two indexed EBSD patterns using the orthorhombic structure model by Burkhardt et al. [5].